A Novel Slurry-Based Biomass Reforming Process

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Project ID #
PD 14

Overview

Timeline

- 1 May 2005
- 31 Oct 2008
- 2%

Budget

- Total project funding
  - $2.9 million, DoE
  - $737k, cost share
- $0, FY04
- $300K, FY05

Barriers

- Barriers:
  - V. Feedstock Cost and Availability
  - W. Capital costs and efficiency of technology
- Barriers Addressed
  - Technology Energy Efficiency
  - Capital Cost
  - Feedstock Flexibility

Partners

- University of North Dakota Environment Energy Research Center

Biomass Slurry Reforming Objectives

DOE: $1.75 kg 99.9+% H_2 with an LHV efficiency of 50%

1. Determine LHV Efficiency Using HYSYS
   - Major efficiency determinants and impact of catalyst efficiency/selectivity
   - Required hydrolysis rate per in unit input energy
   - Capital and energy cost of intermediate hydrogenation step

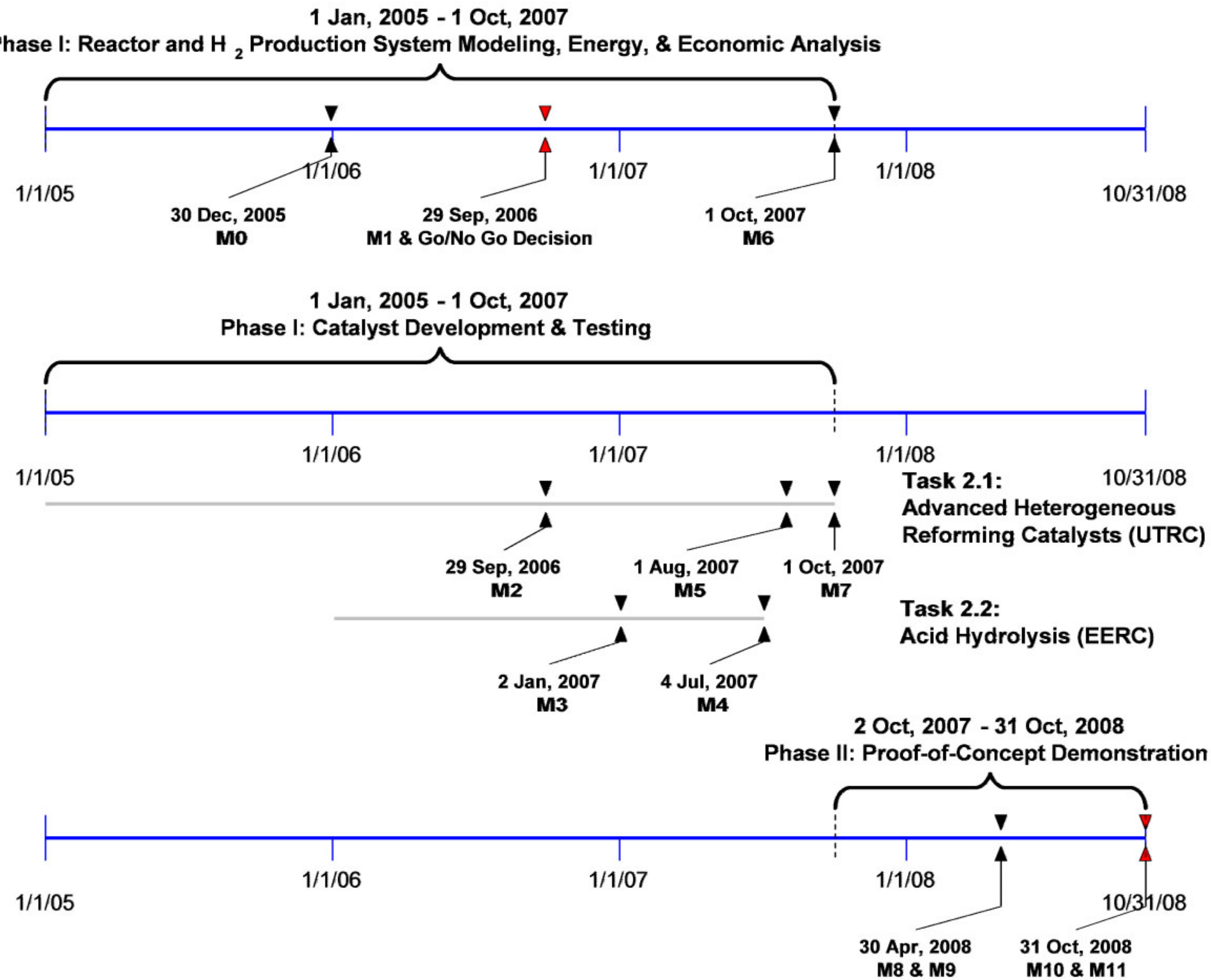
2. H_2 Cost via H2A Spreadsheet: Plant Cost, Rate of Return & Feedstock Costs

3. If DOE Cost and Efficiency Targets Can Be Met, Commence Next Phase
   - Optimum hydrolysis conditions: Energy and Capital Cost
   - Hydrolysis product chemical composition and physical properties
     - Sugar identification and concentrations
     - Identification and quantification of low molecular weight organics
     - Solubility, AMW and surfactant/foaming properties of lignin fraction
   - Catalysis discovery and testing

4. Micro-scale continuous operation of membrane reformer with batch hydrolysis
   - ~500 hr catalyst performance test
   - Collection of material and heat balance data important for plant design

5. Final Economic and Energy Analysis for Final Report

Project Schedule



Approach: Biomass Slurry to Hydrogen Concept

Slurry of ~ 10 % Ground Biomass (Wood) in Dilute Acid

44% cellulose
19% hemicellulose
13% "other"
23% lignin
<1% "ash"
<1% protein

1 or more Hydrolysis Steps

Reformer Feed

~41% soluble C_6 and $(C_6)_n$ "sugars"
~18% soluble "C_5" sugars
~10% "reformable others"
~31% lignin+cellulose fragments etc.

Hydrolysis targets

High Selectivity Pt-MM rafts on engineered nano-structured oxide like $Ti_{[1-(x+y)]}Dp1_xDp2_yO_2$

Preferential RCHO Hydrogenation Catalysts

Optional Sugar Hydrogenation

~59% sugar alcohols
~10% "reformable others"
~31% lignin + cellulose fragments, etc.

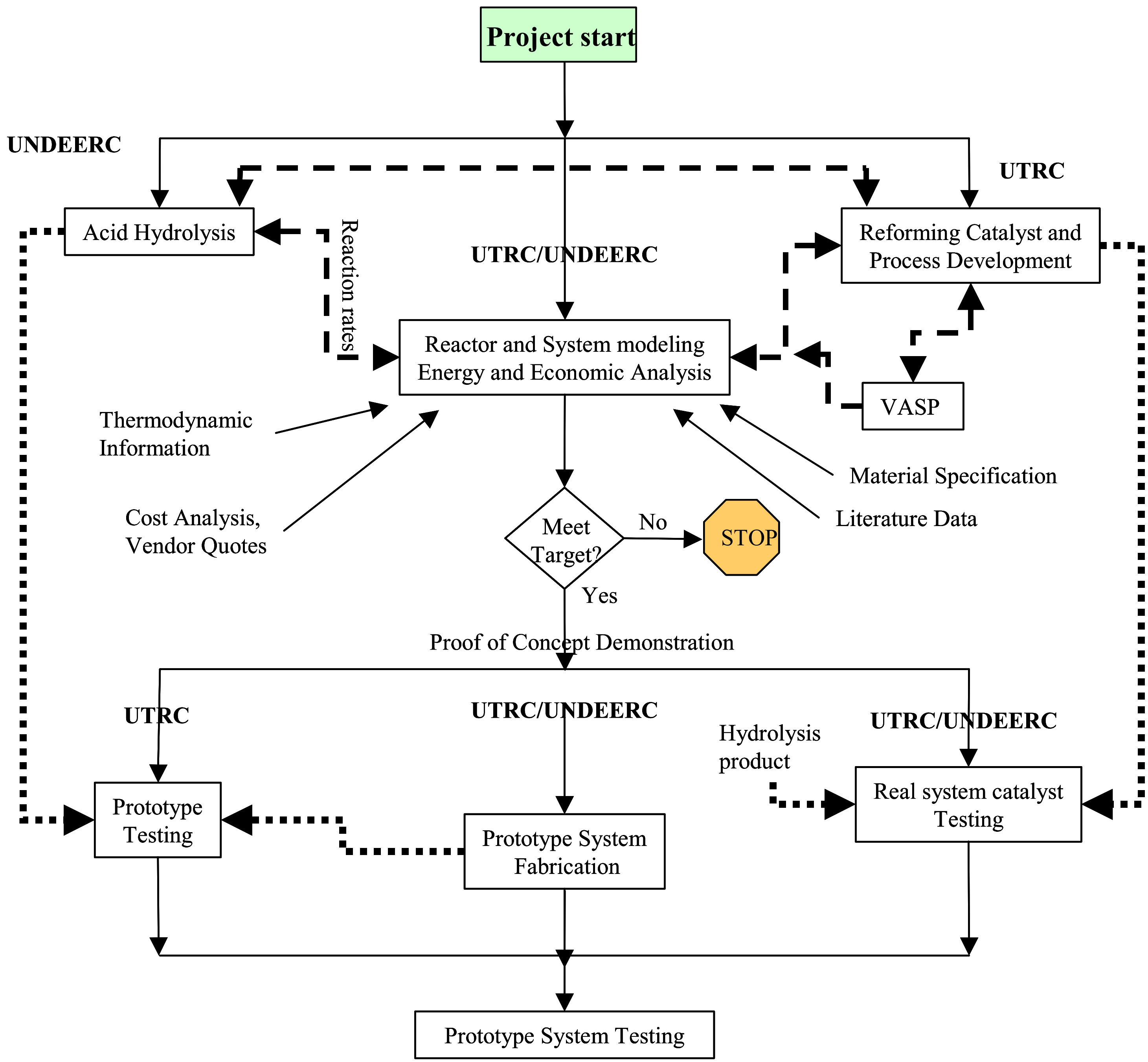
Only if advanced catalysts seem unlikely reach g H_2 / kg feed goals

~83 g 99.9+ H_2 / kg dry Feed Recovered Through Membrane

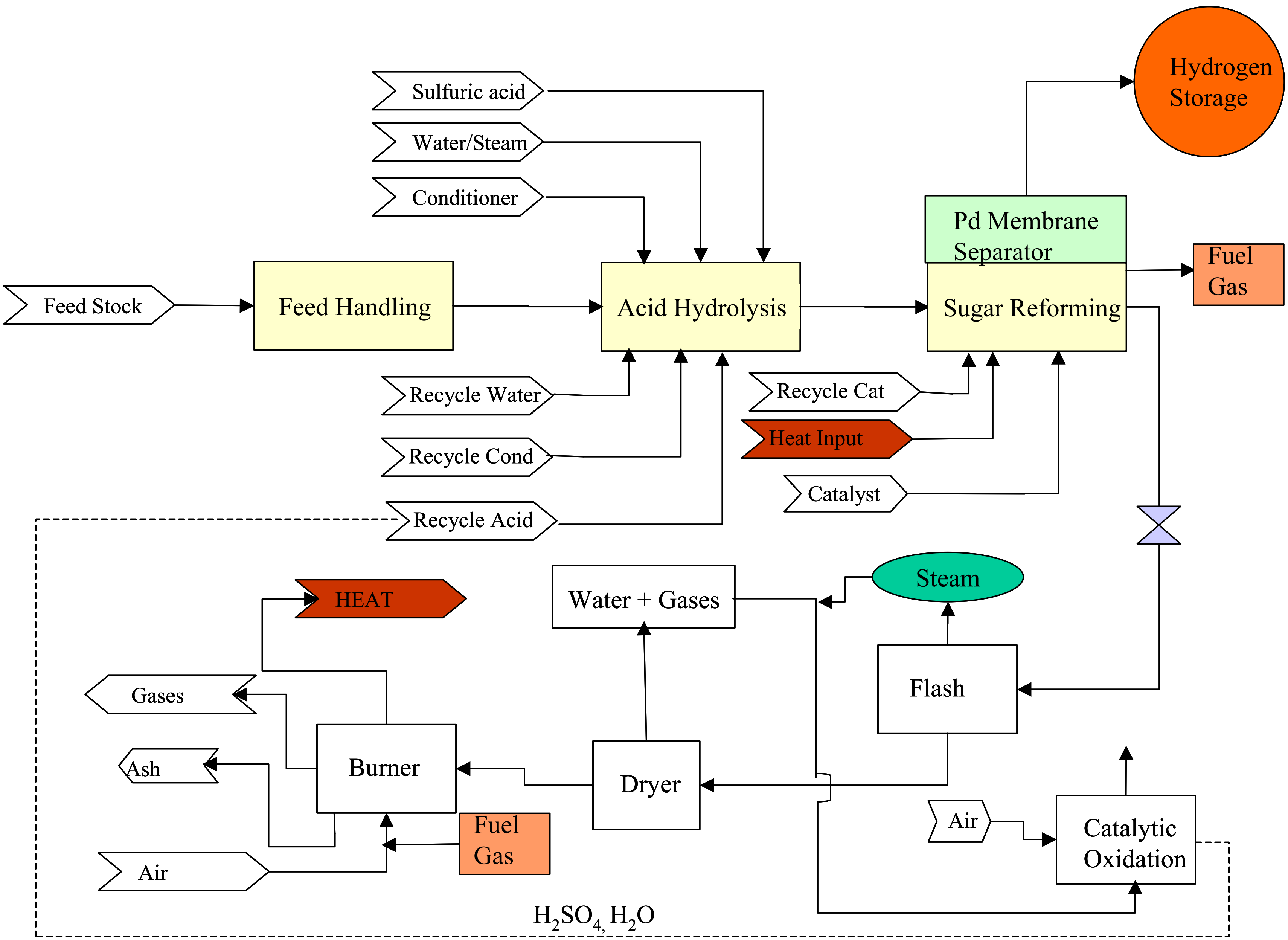
~9 g H_2 or Equivalent as fuel gas
~300 g Lignin and other fuel
~1 kg CO_2

Pt-Re/Ce $_{[1-(x+y)]}Zr_xDp_yO_2$ WGS Catalysts have high activity and very low CH_4 make

Original Project Plan Overview

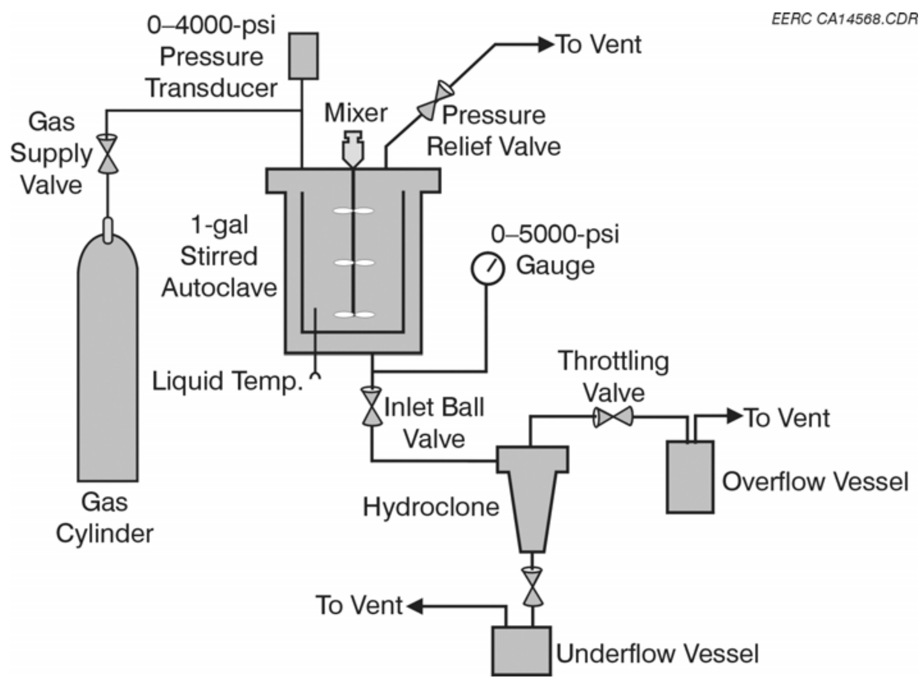


Approach: Initial Process Inputs and Outputs



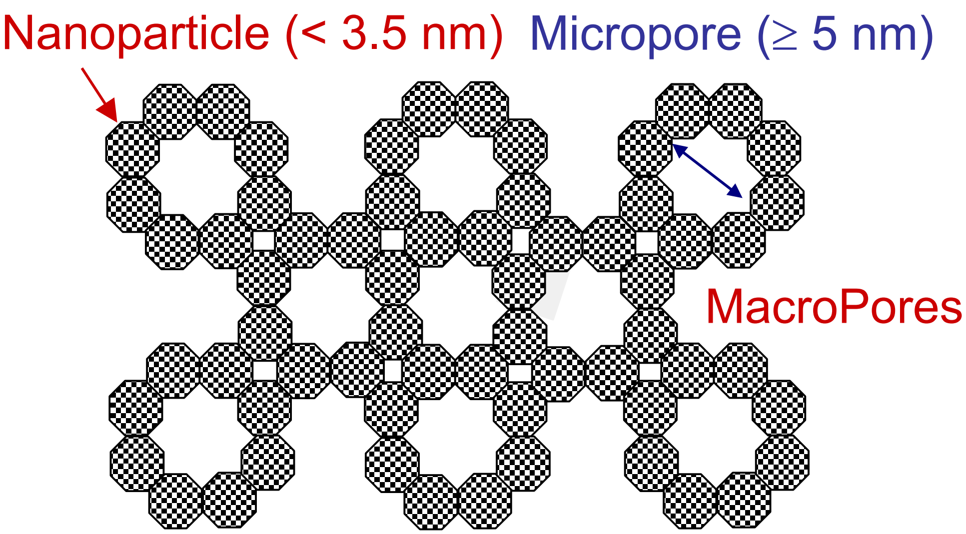
Approach: Experimental Design to Optimize Hydrolysis

- Overall efficiency depends on optimizing hydrolysis energy / acid requirements
  - Lower acid concentration
    - + Less expensive alloys etc.
    - + Higher SA & activity reforming catalysts = smaller reforming reactors
    - + Less unnecessary chemical degradation = higher H_2 yield
  - Lower Temperature
    - + Increased residence time thus larger volumes and increased costs
    - + Lower autogenous steam pressures = lower capital costs
    - + Less expensive alloys etc.
    - + Less dehydrogenation etc. = higher H_2 yields
- Poplar assumed to be initial feed; grinding energy similar to mechanical pulping
- Input data for refined economic and efficiency model



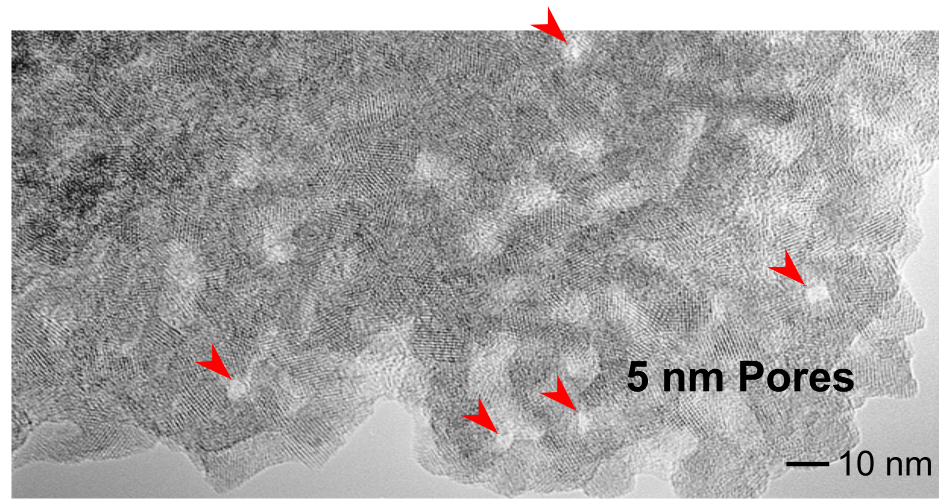
Nano-Engineered Noble Metal / Doped Metal Oxide Catalyst

Design & synthesize active oxide structure to maximize accessible sites/vol.



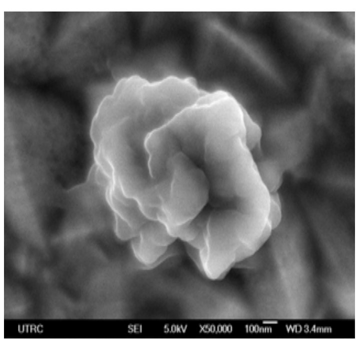
Conceptual Porous Metal-Oxide Framework Shown in 2D

Self assembly used to create high surface area, large pore thermally stable active oxide support with 100% dispersed 2 wt% Pt based mixed metal clusters

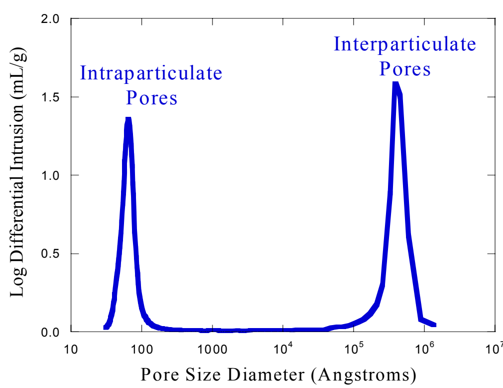


Conceptual Structure Realized

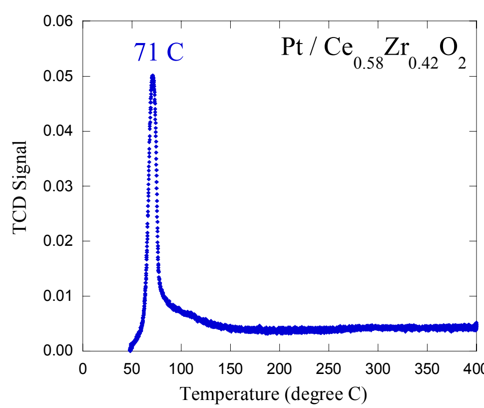
Fractal Morphology



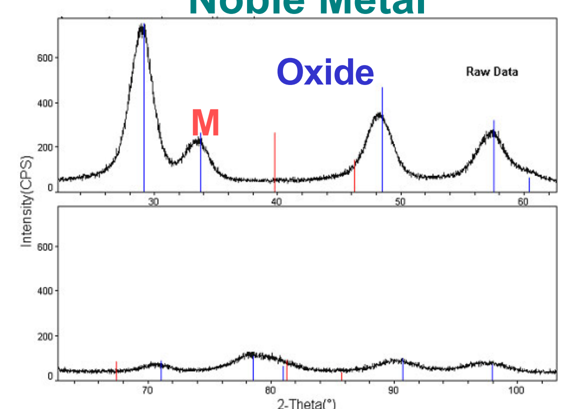
Large, Bimodal Pore Structure



Low Temperature Reducibility



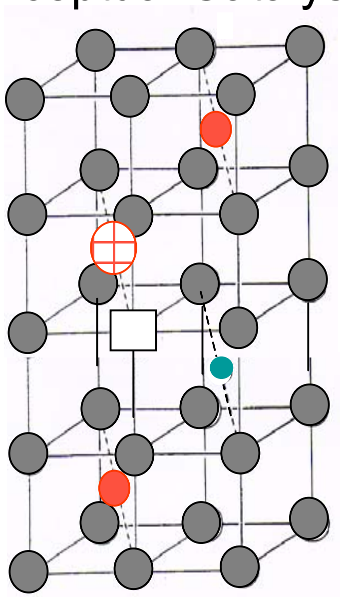
100% Dispersed Noble Metal



UTRC Catalyst Discovery Approach

Atomistic catalyst design, synthesis, characterization, reaction studies & kinetic analysis

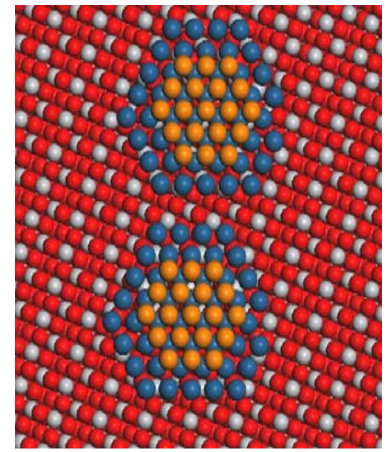
Conceptual Catalyst Design



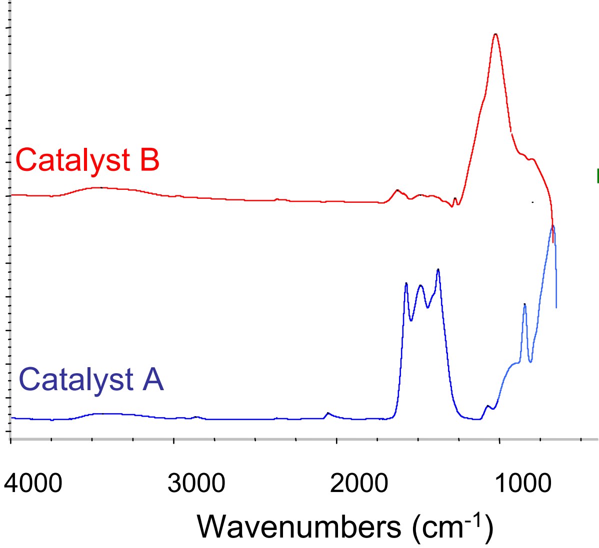
Catalyst Synthesis

High active surface area
Nanocrystalline structure
~100% NM dispersion

Quantum Mechanical Atomistic Modeling for advanced catalyst design



Characterization



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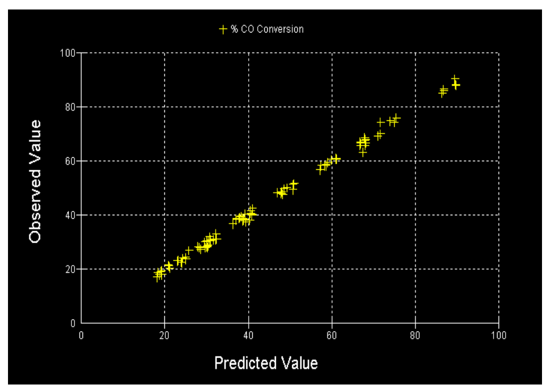
Kinetic Expressions Derived From Reaction Data



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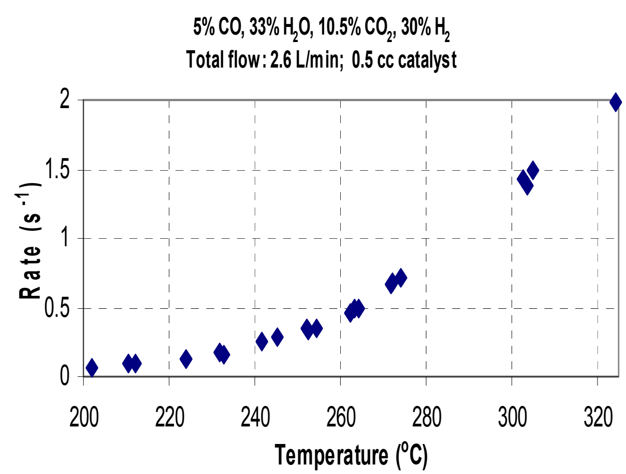
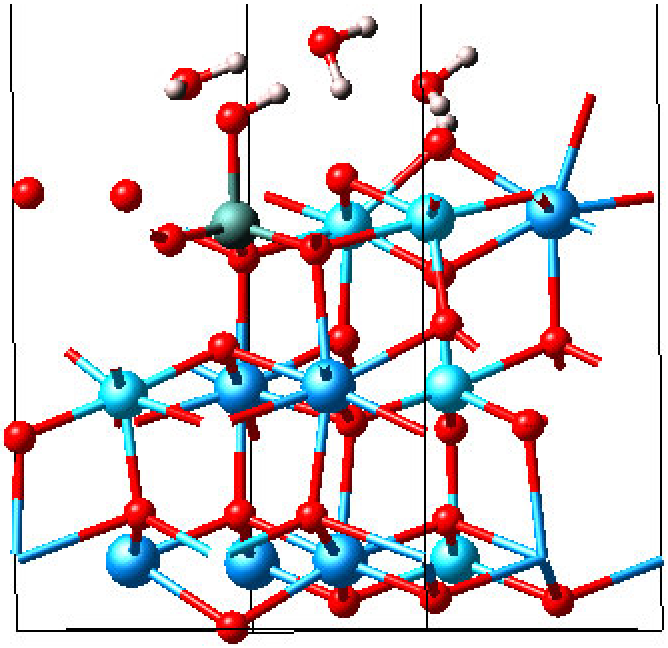
Superior Performance



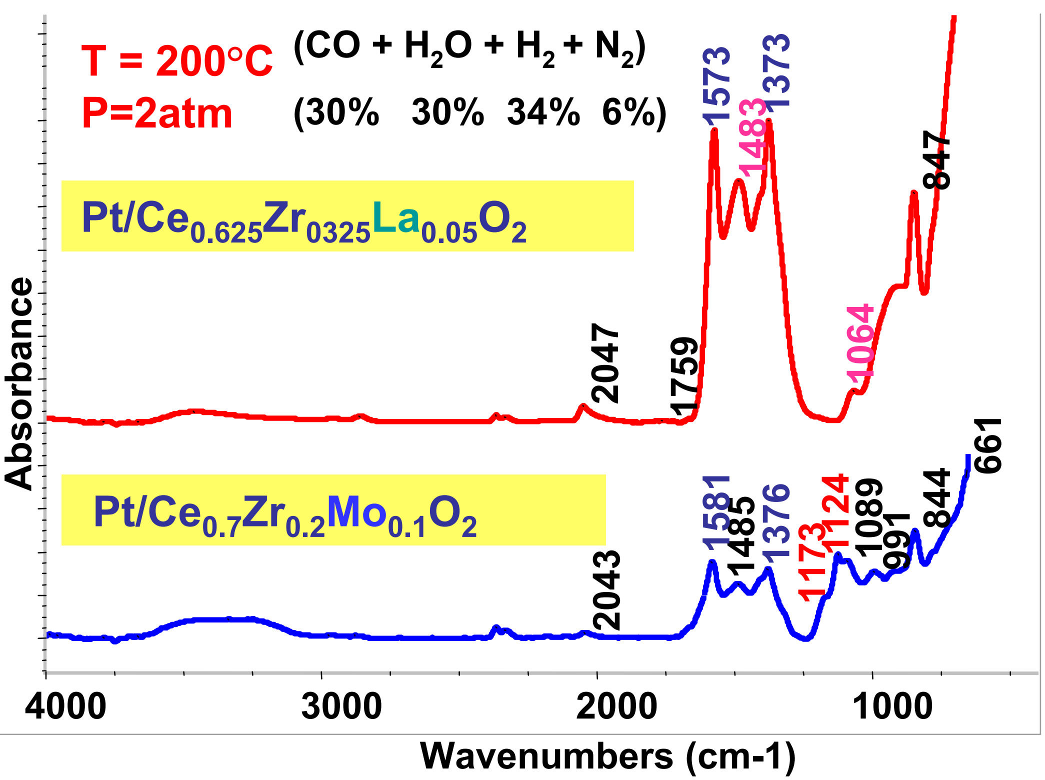
VASP Modeling Insights Led To Better Catalysts

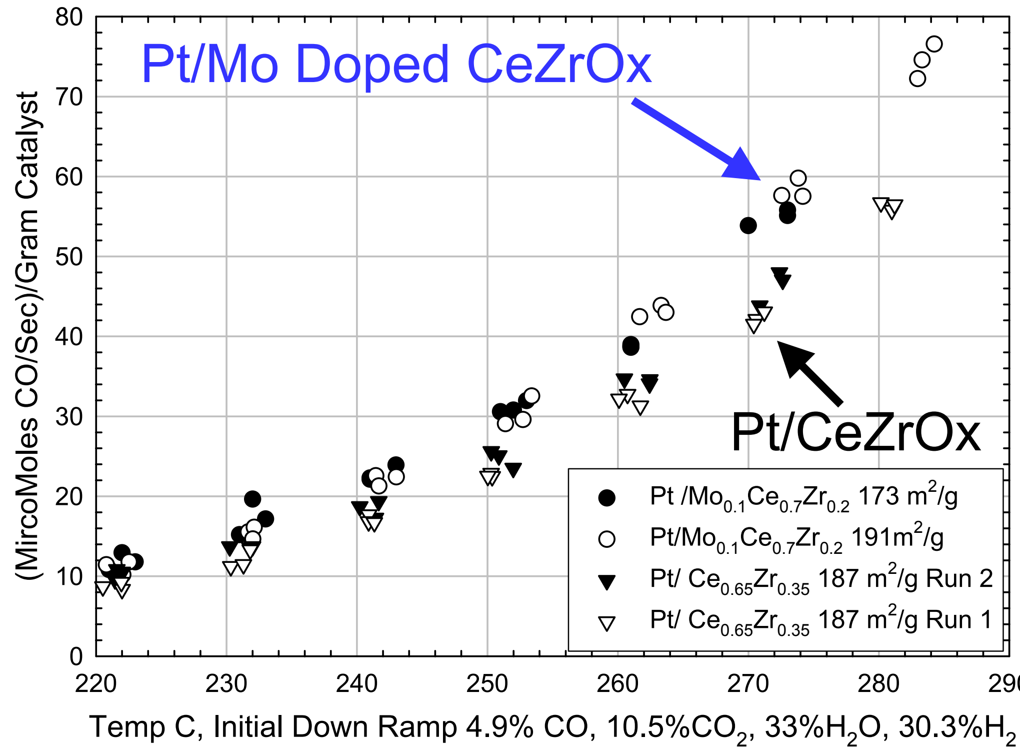


Calculated Coupled Enthalpies

$$Dp_xCe_{12-(x+y)}Zr_yO_{24} \rightarrow Dp_xCe_{12-(x+y)}Zr_yO_{23} + O$$

Oxide Slab	$H_2 + O \rightarrow H_2O$ kJ/Mole	$CO + O \rightarrow CO_2$ kJ/Mole
$Ce_{12}O_{24}$	-154.5	-222.4
$Ce_7Zr_5O_{24}$	-154.5	-222.1
$TaCe_6Zr_5O_{24}$	77.2	9.6
$MoCe_6Zr_5O_{24}$	48.3	-19.3

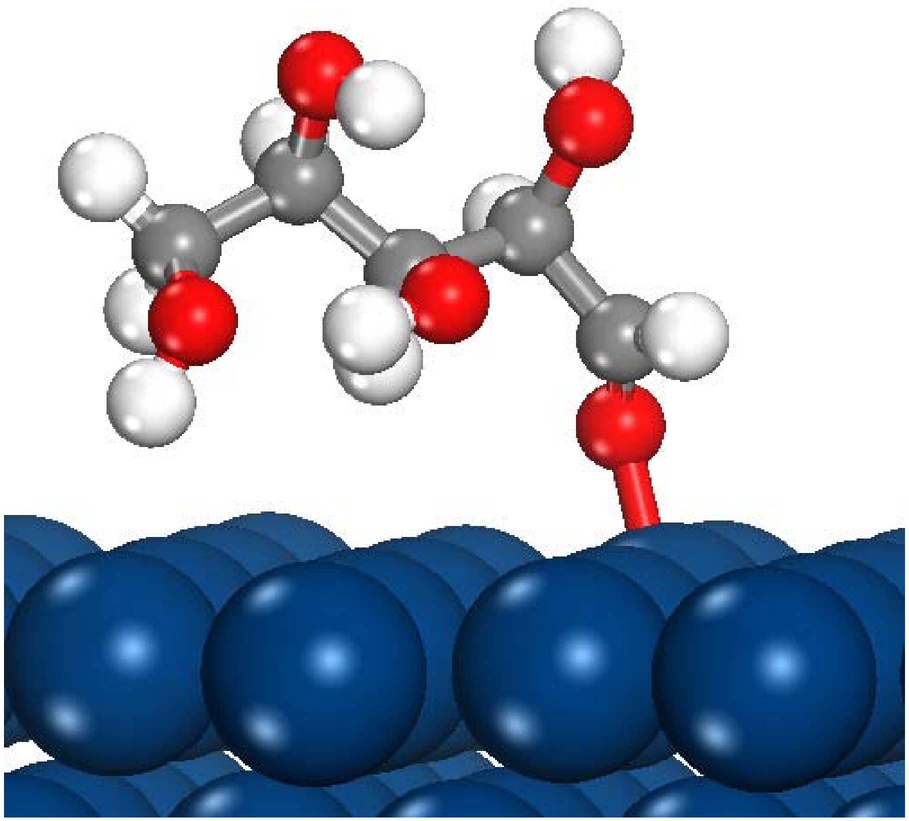


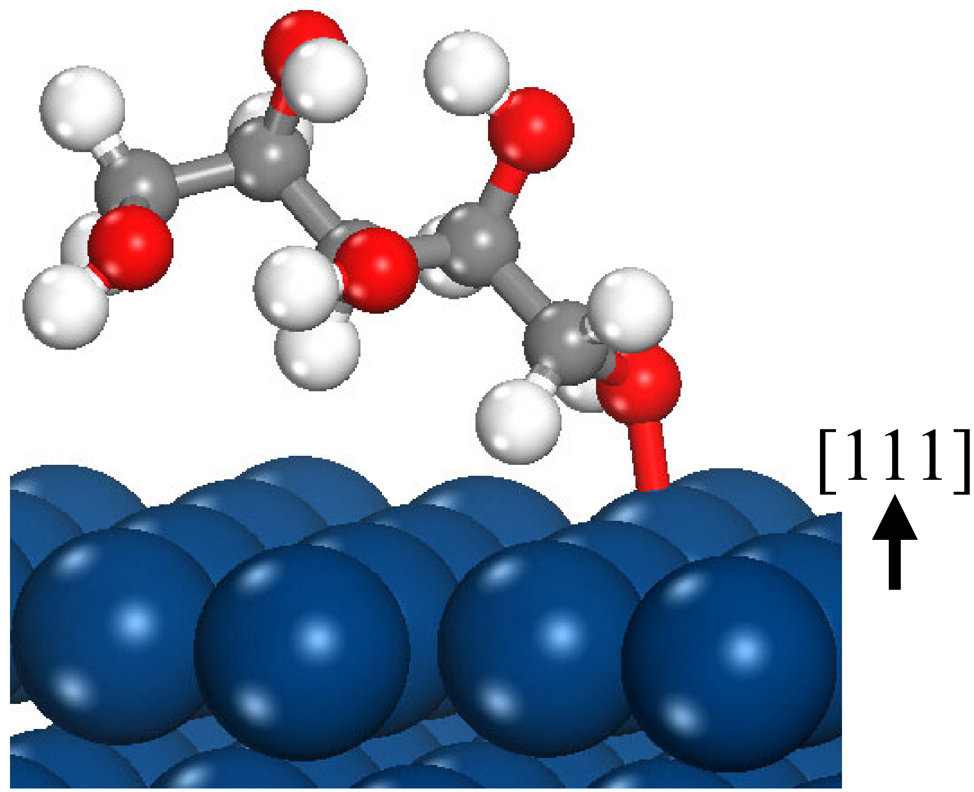


Higher Activity Catalyst w Similar Pt & SA

Xylose Adsorbs More Strongly Than Xylitol on Pt(111)

Aldehyde O forms stronger bond than terminal alcohol O





O C H Pt

Xylose/Pt(111)

Xylitol/Pt(111)

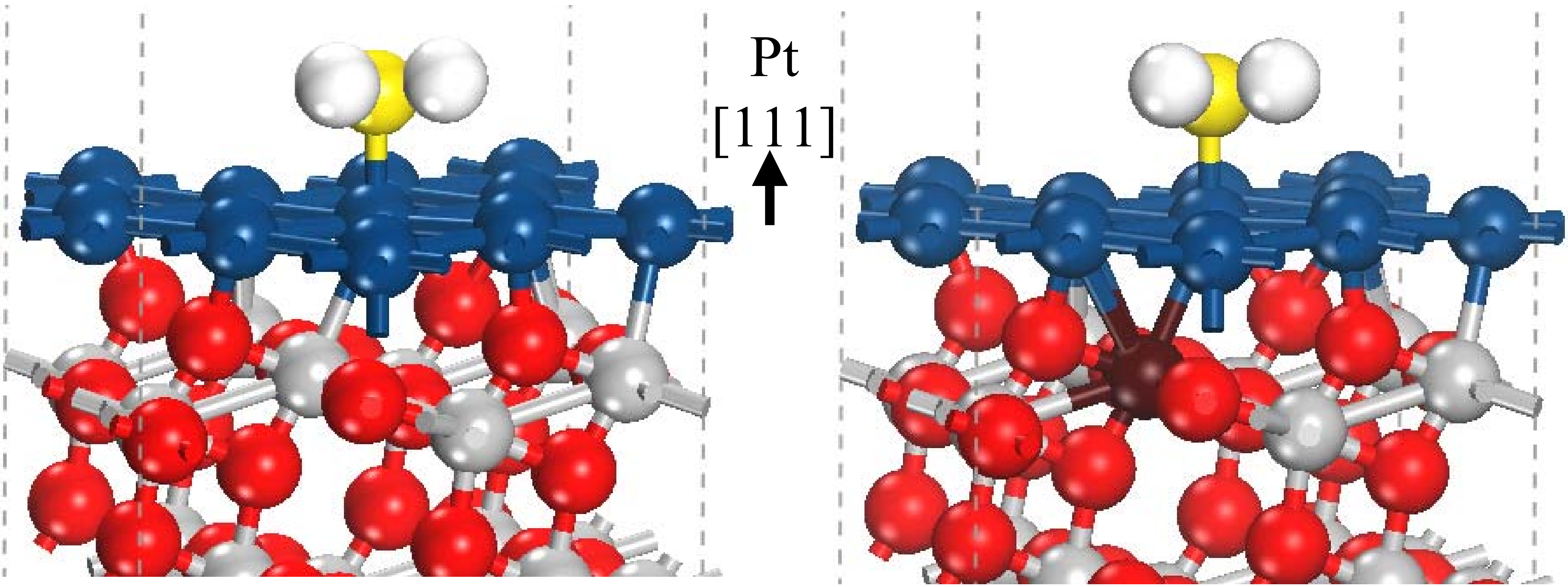
Binding Energy = -92 kJ/mole

Binding Energy = -65 kJ/mole

Negative binding energy indicates exothermic process

Ce Dopant in TiO_2 Decreases H_2S-Pt Binding 16%

- Early results for Pt raft system, before full relaxation
- Anatase (101) TiO_2 with and without Ce

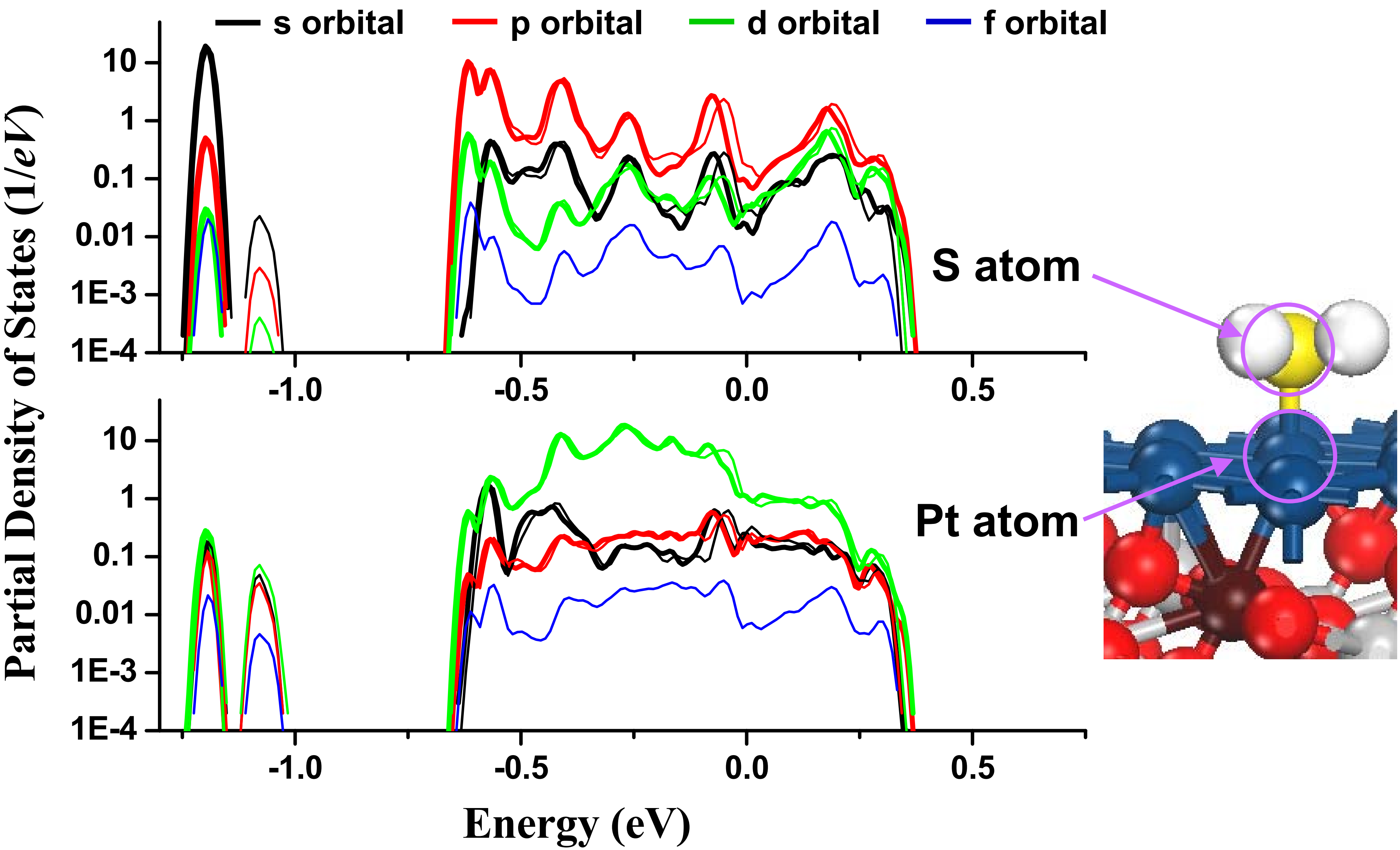


$Pt(111)_{1ML}/AnataseTiO_2(101)$ — Binding Energy -106.53 kJ/mole

$Pt(111)_{1ML}$/4.2a% Ce_Anatase_$TiO_2(101)$ — Binding Energy -89.50 kJ/mole

O Ti H S Pt Ce

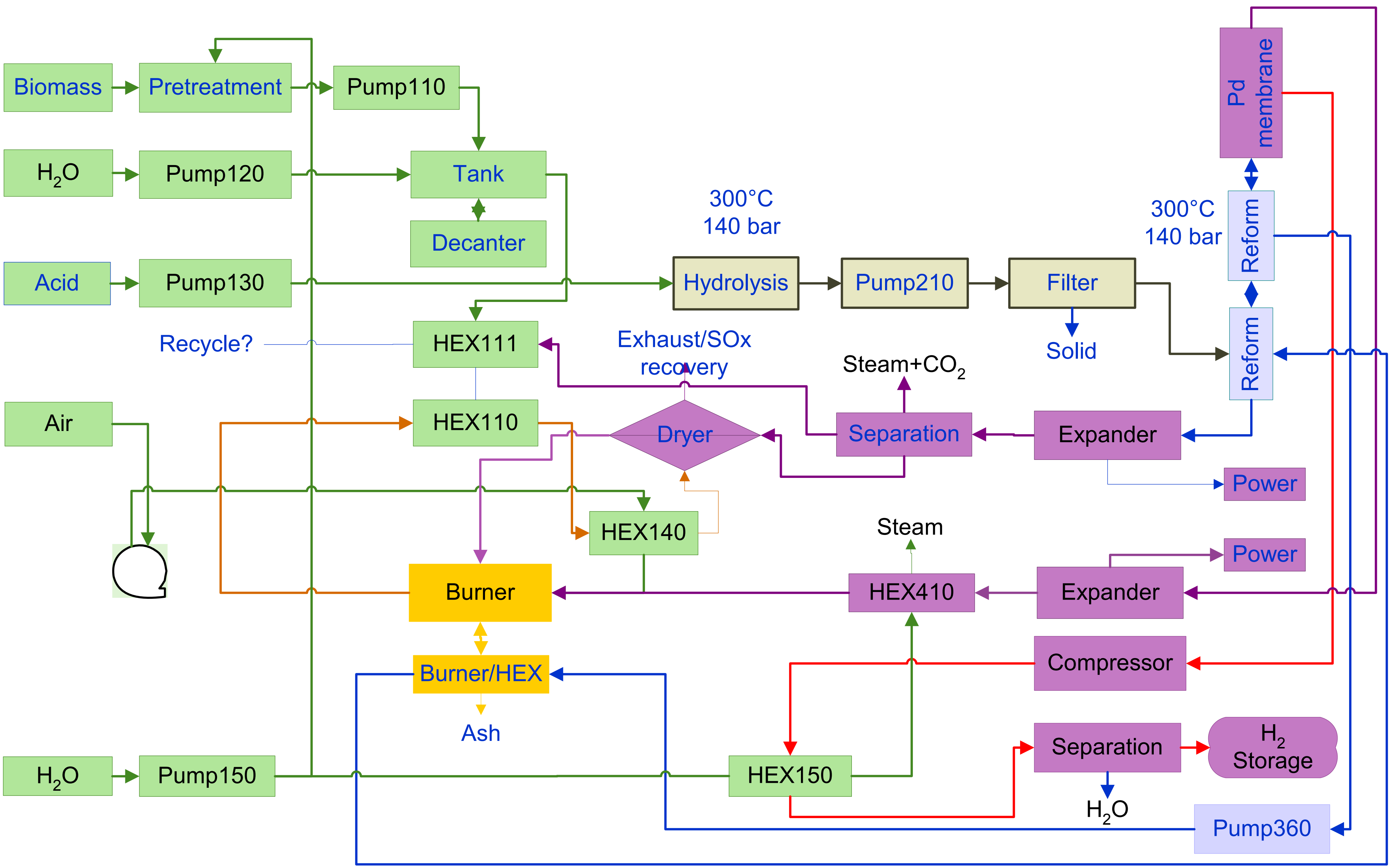
Oxide Dopant Shifts Pt & S DOS to Higher Energy



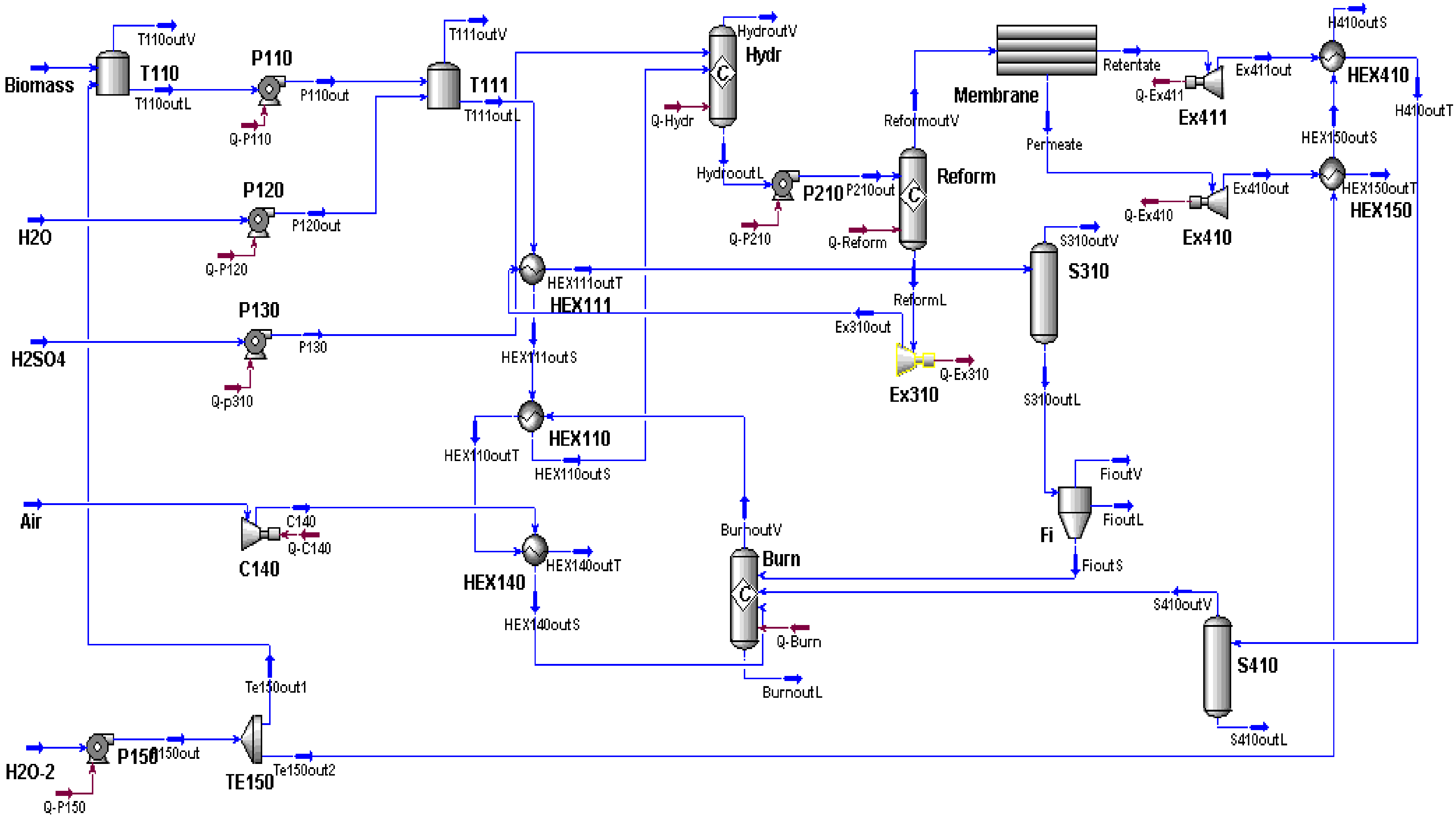
Thick line
Pt(111)$_{1ML}$/TiO$_2$(101)

Thin line
Pt(111)$_{1ML}$/4.2a% Ce in TiO$_2$(101)

Progress: Conceptual Process Flow Diagram



Progress: Current HYSYS Process Flow Diagram



Future Work

- FY 2005:
  - Initial feasibility analysis of a 2000 ton/day (dry) plant design showing a viable path towards the DOE's 2010 efficiency (50% LHV) and cost ($1.75/kg H_2) targets.
  - Low-level construction of catalyst synthesis & testing infrastructure

- FY 2006:
  - Is there a preliminary 2000 ton/day (dry) biomass plant design that could reach the DOE's 2010 efficiency (50% LHV) and cost ($1.75/kg H_2) targets?
  - **GO/NO GO decision**.
  - Demonstrate an acid tolerant, model sugar solution reforming catalyst
    - + Promising kinetics and selectivity
    - + Path for cost-effective scale up (mass production) exists
  - Identify preliminary hydrolysis conditions at UND-EERC and hydrolyzed product chemical composition and physical properties

Future Work

- FY 2007:
  - Demonstrate effective hydrolysis conditions for actual biomass system and a path to scale-up for a viable plant design
  - Demonstrate in the lab a potentially long lived, cost effective liquid phase biomass slurry reforming catalyst giving ~0.1 moles H_2/Total Pt equivalent-second
  - Demonstrate that a plant designed with experimentally determined hydrolysis and reforming rates and conditions meets 50% LHV efficiency and \$1.75 /kg H_2
  - Demonstrate wash coating of active catalyst on to selected support

- FY 2008:
  - Identify optimum hydrolysis conditions
  - Demonstrate wash-coated reforming catalyst with actual hydrolyzed biomass
  - Design, build, test and deliver proto-type continuous micro-scale reforming reactor to UND-EERC
  - Complete 500 hrs of reformer operation and collect data important to full scale pilot unit design
  - Estimate H_2/kg cost and LHV efficiency using 2000 T/day plant design finalized with actual batch hydrolysis and continuous micro-scale reforming reactor data.

Hydrogen Safety

The most significant hydrogen hazard associated with this concept is the 10% H_2 content of the up to 2000 psig process gas.

Hydrogen Safety

Our Approach to deal with the hazard in the laboratory is:

- H_2/Flammable gas detectors and ventilation interlock
  - System alarms if > 10% LFL (0.4% H_2) detected
  - All heater power and flammable gas flows shut off if either >25% of lower flammable limit (1% H_2) detected, or drop in ventilation rate
  - System design limits flammable gas flows to <10% of lower flammable limit based on measured ventilation rate

Hydrogen Safety

Our Approach to deal with the hazard in the proposed micro-scale demonstration unit is:

- Multiple H_2/Flammable gas detectors
- System alarms if >10% LFL (0.4% H_2) detected
- All heater power and flammable gas flows shut off if >25% of lower flammable limit (1.0% H_2) detected at unit.
- N_2 purging of all potential sources of ignition